

**PAT-NO:** JP408092321A  
**DOCUMENT-IDENTIFIER:** JP 08092321 A  
**TITLE:** CRYSTALLINE POLYPROPYLENE  
**PUBN-DATE:** April 9, 1996

**INVENTOR-INFORMATION:**

<b>NAME</b>	<b>COUNTRY</b>
ARAMAKI, MASAAKI	
ITO, MIKI	

**INT-CL (IPC):** C08F110/06 , C08F004/658

**ABSTRACT:**

**PURPOSE:** To obtain a crystalline polypropylene excellent in rigidity, heat resistance and surface hardness.

**CONSTITUTION:** This crystalline polypropylene has 0.1-1000g/10min melt flow rate, >4 to <10 molecular weight distribution, ≥94% isotactic pentad fraction, ≥40% quantitative ratio of the crystalline phase determined by the pulse NMR method and T<sub>2i</sub> and T<sub>2a</sub> ( $\mu$ sec) spin-spin relaxation times of the interfacial and amorphous phases in a relationship of T<sub>2a</sub>-T<sub>2i</sub>≤200.

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**DERWENT-** 1999-226219

**ACC-NO:**

**DERWENT-** 199922

**WEEK:**

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**TITLE:** Ethylene polymer for forming films, pipes - is an ethylene homopolymer or a copolymer containing ~a- olefin of specific carbon number, that satisfies specific conditions

**PATENT-ASSIGNEE:** ASAHI KASEI KOGYO KK[ASAHI]

**PRIORITY-DATA:** 1997JP-0227008 (August 11, 1997)

**PATENT-FAMILY:**

<b>PUB-NO</b>	<b>PUB-DATE</b>	<b>LANGUAGE</b>	<b>PAGES</b>	<b>MAIN-IPC</b>
JP 11060634	AMarch 2, 1999	N/A	009	C08F 010/02

**APPLICATION-DATA:**

<b>PUB-NO</b>	<b>APPL-DESCRIPTOR</b>	<b>APPL-NO</b>	<b>APPL-DATE</b>
JP 11060634A	N/A	1997JP-0227008	August 11, 1997

**INT-CL (IPC):** C08F004/645, C08F010/02 , C08F210/16

**ABSTRACTED-PUB-NO:** JP 11060634A

**BASIC-ABSTRACT:**

NOVELTY - The ethylene polymer which is an ethylene homopolymer or a copolymer containing alpha -olefin with 3-20 C, satisfies some specific conditions.

DETAILED DESCRIPTION - The ethylene polymer satisfies the following conditions: (A) the melt indices in 2.16 kg load at 190 deg. C are 0.001-1000 g/10 min, (B) the density is 0.90-0.985 g/cm<sup>3</sup>, (C) the ratio of molecular weight distribution measured by gel-permeation chromatography is 3-7, (D) the ratio T<sub>2a</sub>/T<sub>2c</sub> measured by <sup>1</sup>H pulse nuclear magnetic resonance (NMR) at 40 deg. C is 7.2 or less, where T<sub>2c</sub> is spin relaxation time (microsecond) for the crystal part and T<sub>2a</sub> is spin relaxation time (microsecond) for the amorphous part.

USE - For pipes and films.

ADVANTAGE - The ethylene polymer has a constrained amorphous part and has improved moldability and ductility.

**CHOSEN-** Dwg. 0/0

**DRAWING:**

**TITLE-** ETHYLENE POLYMER FORMING FILM PIPE ETHYLENE HOMOPOLYMER  
**TERMS:** COPOLYMER CONTAIN OLEFIN SPECIFIC CARBON NUMBER SATISFY  
SPECIFIC CONDITION

**DERWENT-CLASS:** A17 A88

**CPI-CODES:** A04-G06A; A12-H02; A12-S06;

**ENHANCED-** Polymer Index [1.1] 018 ; H0000 ; R00326 G0044 G0033 G0022  
**POLYMER-** D01 D02 D12 D10 D51 D53 D58 D82 ; S9999 S1285\*R ; S9999  
**INDEXING:** S1581 ; S9999 S1661 ; P1150 ; P1161 Polymer Index [1.2]  
018 ; H0022 H0011 ; R00326 G0044 G0033 G0022 D01 D02 D12  
D10 D51 D53 D58 D82 ; G0033\*R G0022 D01 D02 D51 D53 D58  
D83 D84 D85 D86 D87 D88 D89 D90 D91 D92 D93 D94 ; S9999  
S1285\*R ; S9999 S1581 ; S9999 S1661 ; P1150 Polymer Index  
[1.3] 018 ; ND04 ; B9999 B3601 B3554 ; B9999 B4831\*R  
B4740 ; B9999 B5107\*R B4977 B4740 ; B9999 B3623 B3554 ;  
B9999 B4137 B4091 B3838 B3747 ; Q9999 Q8731 Q8719 ; B9999  
B4784 B4773 B4740 ; B9999 B5232 B4740 Polymer Index [1.4]  
018 ; D01 A1 3A ; H\* B\* 3A ; C999 C168 ; C999 C293 Polymer  
Index [1.5] 018 ; D01 D15 D13 D75 D54 D51 D59 D56 D62 D61  
D68 Ti 4B Tr D57 D55 ; C999 C033 C000 ; C999 C293

**SECONDARY-ACC-NO:**

**CPI Secondary Accession Numbers:** C1999-066553

## [Original papers 1997]

H. Ishida, H. Kaji and F. Horii, Solid-State NMR Analyses of the Structure and Chain Conformation of thermotropic Liquid Crystalline Polyurethane Crystallized from the Melt through the liquid Crystalline State, *Macromolecules*, 30, 5799-5803 (1997).

Solid-state  $^{13}\text{C}$  NMR analyses of the structure and chain conformation have been performed for a thermotropic liquid crystalline polyurethane that was polymerized from 3,3'-dimethyl-4,4'-biphenydiyl diisocyanate, 1,10-decanediol, and 1-hexanol with a mole ratio of 25/24/2. This sample was crystallized by cooling from the isotropic melt through the liquid crystalline state at a rate of 1°C/min. DSC thermograms of the cooling scan exhibit only one endothermic peak, whereas two exothermic peaks corresponding to the melting and isotropic points appear in the heating scan. However, the polarizing optical microscopic observation confirms that the crystallization occurs almost at the same time after the appearance of the liquid crystalline phase, although some part of the liquid crystalline phase is frozen without crystallization.  $T_{1\text{C}}$  analyses reveal that the sample contains three components with different  $T_{1\text{C}}$  values, which correspond to the crystalline, medium, and noncrystalline regions. From the line shape analyses of these three components are found to be in the same all trans conformation. In contrast, the methylene sequence for the noncrystalline component, which is ascribed to the frozen liquid crystalline component, is in the alternate trans and trans-gauche exchange conformation, probably reflecting the conformation that exists in the liquid crystalline state.

H. Kaji and F. Horii, One- and Two-Dimensional Solid-State  $^{13}\text{C}$  NMR Analyses of the Solid Structure and Molecular Motion of Poly( $\epsilon$ -caprolactone) Isothermally Crystallized from the Melt, *Macromolecules*, 30, 5791-5798 (1997).

The crystalline-noncrystalline structure and molecular motion of poly( $\epsilon$ -caprolactone) (PCL) isothermally crystallized from the melt have been investigated by one-and two-dimensional solid-state  $^{13}\text{C}$  NMR spectroscopy. The  $^{13}\text{C}$  spin-lattice relaxation time ( $T_{1\text{C}}$ ) analysis reveals that the PCL sample contains three components with different ( $T_{1\text{C}}$ ) values, which are assignable to the crystalline, mobile crystalline, and noncrystalline components. By the  $^{13}\text{C}$  spin-spin relaxation time ( $T_{2\text{C}}$ ) analysis, it is found that the noncrystalline component can be further resolved into the crystalline-amorphous interfacial, and amorphous components. The mass fraction of the crystalline, interfacial, and amorphous components are finally determined to be 0.42, 0.30, and 0.28, respectively. In the crystalline region, different molecular mobilities along the methylene quence are suggested through the difference in  $T_{1\text{C}}$  C value for the constituting carbons. More detailed molecular motion in the crystalline region has been

characterized by the analysis of the  $^{13}\text{C}$  chemical shift anisotropy (CSA) in terms of the two-site exchange model.  $^{13}\text{C}$  CSA spectra of the individual carbons are successfully recorded by using the two-dimensional switching angle sample spinning technique. The CSA spectrum of the carbonyl carbon exhibits that the carbonyl carbon is almost in the rigid state or undergoes the jump motion around the molecular chain axis with a jump angle less than  $30^\circ$ . In contrast, methylene carbons exhibit almost axially symmetric CSA spectra, suggesting the rapid jump motions around the molecular chain axis with a jump angle of  $60\text{-}90^\circ$ . Further narrowed CSA spectra, which are still axially symmetric, are observed for the methylene carbons not directly attached to the ester group, suggesting the existence of additional enhanced jump motion around the C-C bonds. Such enhanced molecular motions of the methylene sequence may be due to the distorted nonplanar zigzag chain conformation of PCL in the crystalline region.

A. Hirai, M. Tsuji, and F. Horii, Culture Conditions Producing Structure Entities Composed of Cellulose I and II in Bacterial Cellulose, *Cellulose*, 4, 239-245 (1997).

Culture conditions for the production of Cellulose I and/or II structures have been investigated by transmission electron microscopy using smooth colonies of *Acetobacter xylinum* ATCC23769. Cells prepared from smooth colonies produce the band material composed of Cellulose II in phosphate buffer (pH7) at  $4^\circ\text{C}$ . In contrast, the same cells produce the normal twisting ribbons of Cellulose I when the incubation temperature is raised to  $28^\circ\text{C}$ . The band material is also produced at  $4^\circ\text{C}$  in 2% buffered glucose solution and in standard Hestrin-Schramm medium.

F. Horii, K. Masuda, and H. Kaji, CP/MAS  $^{13}\text{C}$  NMR Spectra of Frozen Solutions of Poly(vinyl alcohol) with Different Tacticities, *Macromolecules*, 30, 2519-2520 (1997).

Frozen-state  $^{13}\text{C}$  NMR measurements have been made for different frozen solutions of poly(vinyl alcohol) (PVA) with different tacticities to characterize intramolecular hydrogen bonds. 3-10% frozen aqueous or dimethyl sulfoxide (DMSO) solutions are prepared in a magic angle spinning (MAS) rotor with an O-ring seal, rotating at a rate of about 1 kHz in a CP/MAS probe, by decreasing the temperature to  $-50^\circ\text{C}$ . The CH resonance line of atactic PVA (A-PVA) splits into two lines, lines II and III, in the frozen aqueous solution, suggesting the formation of a small amount of isolated intramolecular hydrogen bonds. In the frozen DMSO solution, such intramolecular hydrogen bonds seem to increase in fraction, and as a result some amount of continuous intramolecular hydrogen bonds, which contributes to line I, may be formed. In contrast, a single resonance line assignable to line III appears for highly isotactic PVA in the frozen DMSO solution, whereas almost the same spectrum as for A-PVA is observed in the frozen aqueous solution. These results indicate that trans and gauche conformations in the triad sequences as well as so-called  $\gamma$ -gauche effect on the chemical shift of the CH carbons

should be critically evaluated to interpret the splitting of the CH resonance line in the noncrystalline frozen state of PVA.

K. Kuwabara, H. Kaji, F. Horii, D. C. Bassett, and R. H. Olley R. H., Solid-State NMR Analyses of the Crystalline-Noncrystalline Structure for Metallocene-Catalyzed Linear Low-Density Polyethylene, *Macromolecules*, 30, 7516-7521 (1997).

Solid-state  $^{13}\text{C}$ -NMR analyses have been performed to obtain information about the crystalline-noncrystalline structure for metallocene-catalyzed linear low-density polyethylene (MLLDPE) isothermally crystallized from the melt.  $^{13}\text{C}$  spin-lattice relaxation time ( $T_{1\text{C}}$ ) and  $^{13}\text{C}$  spin-spin relaxation time ( $T_{2\text{C}}$ ) analyses have revealed that the three components with different  $T_{1\text{C}}$  and  $T_{2\text{C}}$  values exist for MLLDPE, which are assignable to the crystalline, crystalline-amorphous interfacial, and rubbery-amorphous components. Using such differences in  $T_{2\text{C}}$ , we have separately recorded the spectra of interfacial and amorphous components and then resolved the fully relaxed DD/MAS spectrum of MLLDPE into the three components. As a result, it has been found that the thickness of the interfacial region is about 3 nm, in good accord with the previous result for bulk-crystallized high-density polyethylene (HDPE).  $T_{1\text{pH}}$  and  $T_{2\text{C}}$  analyses have also revealed that butyl branches are excluded out from the crystalline region and are almost equally distributed in the crystalline-amorphous interfacial and amorphous regions. It has been also found that the molecular mobility is somewhat more enhanced in the interfacial region for MLLDPE compared with the case for HDPE. The same analysis is applied to Ziegler-Natta-catalyzed LLDPE isothermally crystallized from the melt as well as those quenched samples, and the crystalline-noncrystalline structures of the samples are discussed.

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#### [Reviews 1997]

F. Horii, H. Yamamoto, and A. Hirai, Microstructural Analysis of Microfibrils of Bacterial Cellulose, *Macromol. Symp.*, 120, 197-205 (1997).

This paper reviews mainly our recent investigations of two allomorphs of native cellulose, celluloses I $_{\alpha}$  and II $_{\beta}$ , carried out based on the composite crystal model by high resolution solid state  $^{13}\text{C}$  NMR and electron microscopy. First the distribution of the two allomorphs in nature is described together with some deviations from the simple composite crystal model. Secondly, the influences of polymer additives on the crystallization of the two allomorphs are described in the bacterial system somewhat in detail. On the basis of these results, the mechanism of the crystallization of the two allomorphs is finally discussed also in the bacterial cellulose system.

F. Horii, Bacterial Cellulose—Structural Formation in the Biogenesis, *Kagaku*, 52, 70-71 (1997).

The composite crystal model, in which native cellulose crystals are assumed to be composites of celluloses I <sub>$\alpha$</sub>  and II <sub>$\beta$</sub> , is reviewed according to the historical progress. A hypothetical proposal for the crystallization mechanism of the composite crystals is also described for the bacterial cellulose system.

A. Hirai, M. Tsuji, and F. Horii, Formation of Cellulose II Crystal in Bacterial Cellulose, *Cellulose Commun.*, 4, 21-24 (1997).

By transmission electron microscopy, culture conditions producing structure entities of cellulose I and/ or Cellulose II have been investigated using smooth colonies isolated from *Acetobacter xylinum* ATCC23769. The cells prepared from the smooth colony are found to produce the band material composed of Cellulose II at 4°C in the phosphate buffer of pH 7 and in the standard HS medium. The band material is extruded perpendicularly to the long axis of the cell. In contrast, the same colony yields the normal twisting ribbon of Cellulose I when the incubation temperature is raised to 28°C, and vice versa.

T. Nonaka and F. Horii, New Polymeric Materials as Speaker Cones, *Koubunshi Kakou*, 46, 368-373 (1997).

This article briefly reviews developments of new polymeric materials as speaker cones including newly developed pulp-based speaker cones containing tunicate cellulose.

H. Kaji, Analyses of Conformation and Local Structure of Polymers by Two-Dimensional Solid - State NMR Method, *Kaigai Koubunshi Kenkyu*, 43, 107-108 (1997).

H. Kaji, T. Tai, and F. Horii, Two-Dimensional solid-state NMR Analyses of Medium-range Molecular Motion of Polymers, *Proc. Soc. Solid-State NMR Mater.*, No. 21, 35-39 (1997).

This article reviews advanced two-dimensional solid-state NMR spectroscopies to analyze molecular motions of polymers with 10<sup>-1</sup> - 10<sup>5</sup>Hz; <sup>13</sup>C chemical shift anisotropies (CSA) analyses measured by two-dimensional switching angle sample spinning (SASS) or by magic angle turning (MAT) as well as one-and two-dimensional <sup>2</sup>H NMR analyses are briefly described.

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[Books 1997]

F. Horii, Ed., Special Issue of Cellulose, 4, No.2, 1997.

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